Polarized spectroscopy of Sm^{3+} ions in monoclinic $KGd(WO_4)_2$ crystals

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Abstract. We report on a polarization-resolved spectroscopic study of Sm^{3+}-doped monoclinic $KGd(WO_4)_2$ crystals. The transition probabilities for Sm^{3+} ions were calculated using a modified Judd-Ofelt theory. For the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition in the red spectral range, the stimulated-emission cross-section is 5.59×10^{-21} cm² at 649.0 nm (for light polarization $\boldsymbol{E} \parallel N_p$) and the luminescence lifetime of the $^4G_{5/2}$ state is 719 μs (0.4 at.% Sm^{3+}-doping). Sm:$KGd(WO_4)_2$ is promising for orange and red lasers.

1 Introduction

Trivalent samarium ions (Sm^{3+}) possess an electronic configuration of [Xe]$4f^5$, with a group of lower-lying ^6F_J and ^6H_J multiplets ($^6H_{5/2}$ is the ground-state) and a metastable state $^4G_{5/2}$. This energy-level structure gives rise to multiple emissions in the visible and near-infrared, among which the transitions in orange ($^4G_{5/2} \rightarrow {}^6H_{7/2}$), red ($^4G_{5/2} \rightarrow {}^6H_{9/2}$) and deep-red ($^4G_{5/2} \rightarrow {}^6H_{11/2}$) are of main interest for the development of visible laser sources [1]. So far, only a few Sm^{3+}-doped crystals (*e.g.*, $LiYF_4$ and $SrAl_{12}O_{19}$) were studied in this regard. Monoclinic double tungstates represent a family of laser host matrices being very suitable for doping with trivalent rare-earth (RE^{3+}) ions. They feature high absorption and emission cross-sections of RE^{3+} ions with a strong polarization anisotropy and weak concentration quenching of luminescence. Visible laser emission was recently achieved from a stoichiometric $KEu(WO_4)_2$ crystal [2].

In the present work, we report on a polarization-resolved spectroscopic study of Sm^{3+} ions in monoclinic potassium gadolinium double tungstate ($KGd(WO_4)_2$) crystal, for the first time, with the goal of developing novel gain media for visible lasers.

2 Crystal growth

A series of Sm^{3+}-doped $KGd(WO_4)_2$ crystals was grown by the Top-Seeded Solution Growth (TSSG) method using $K_2W_2O_7$ as a solvent and [010]-oriented seeds. Three doping levels were studied, 0.4, 0.8 and 20 at.% of Sm^{3+}. The crystals are monoclinic (sp. gr. C^6_{2h} – $C2/c$). The Sm^{3+} ions replace for the host-forming Gd^{3+} cations (ionic radii: $R_{Gd} = 1.053$ Å and $R_{Sm} = 1.079$ Å for VIII-fold oxygen coordination) in a single type of sites (C_2). The Sm:$KGd(WO_4)_2$ crystal is optically biaxial, and its optical properties are described in the optical indicatrix frame N_p, N_m and N_g.

3 Polarized spectroscopy

The polarized absorption cross-section, σ_{abs}, spectra of Sm^{3+} ions in the violet and blue spectral ranges are shown in Fig. 1. The spectra are strongly polarized, with $\boldsymbol{E} \parallel N_m$ being the preferable pump polarization. In the spectral range addressed by commercial 2ω-OPSLs, the maximum σ_{abs} is 0.76×10^{-20} cm² at 487.8 nm corresponding to an absorption bandwidth (FWHM) of only 2.7 nm. This absorption peak corresponds to the spin-forbidden ($\Delta S \neq 0$) $^6H_{5/2} \rightarrow {}^4M_{15/2}$ transition. At shorter wavelengths, an intense absorption band is related to the spin-allowed ($\Delta S = 0$) $^6H_{5/2} \rightarrow {}^6P_{3/2}$ transition. The corresponding σ_{abs} is about an order of magnitude higher, 8.37×10^{-20} cm² at 404.5 nm (FWHM, 0.9 nm).

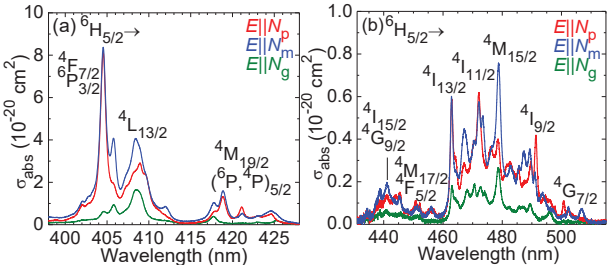

Fig. 1. (a,b) Polarized absorption cross-sections, σ_{abs}, for Sm^{3+} ions in the $KGd(WO_4)_2$ crystal in the blue-violet spectral range.

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Table 1. Probabilities of spontaneous radiative transitions for Sm^{3+} ions in the $KGd(WO_4)_2$ crystal calculated using the Judd-Ofelt theory: λ_{em} – mean emission wavelength, $A_{JJ'}$ – transition probability (ED – electric dipole, MD – magnetic dipole), $\beta_{JJ'}$ - luminescence branching ratios.

$^4G_{5/2} \rightarrow$	λ_{em} (nm)	$\beta_{JJ'}$ (%)	$A_{JJ'}$ (s^{-1})
$^6F_{11/2}$	1355.6	0.05	0.66^{ED}
$^6F_{9/2}$	1156.9	0.8	10.59^{ED}
$^6F_{7/2}$	1026.3	1.0	$12.18^{ED}+1.74^{MD}$
$^6F_{5/2}+^6F_{3/2}+$ $^6H_{15/2}+^6F_{1/2}$	903.0	8.9	$104.3^{ED}+16.75^{MD}$
$^6H_{13/2}$	794.2	0.9	12.82^{ED}
$^6H_{11/2}$	716.3	8.4	114.1^{ED}
$^6H_{9/2}$	655.0	40.2	548.2^{ED}
$^6H_{7/2}$	607.2	33.8	$434.5^{ED}+25.54^{MD}$
$^6H_{5/2}$	564.1	6.0	$49.93^{ED}+31.27^{MD}$

Based on the measured polarized absorption spectra, the 4f – 4f transition probabilities for Sm^{3+} in the $KGd(WO_4)_2$ crystal were calculated using the modified Judd-Ofelt (mJ-O) theory accounting for configuration interaction [3]. The obtained intensity parameters are Ω_2 = 8.027, Ω_4 = 7.210, Ω_6 = 2.322 [10^{-20} cm^2] and α = -0.017 [10^{-4} cm]. The probabilities of spontaneous radiative transitions from the metastable $^4G_{5/2}$ Sm^{3+} state are listed in Table 1. The radiative lifetime, τ_{rad}, of this manifold is 734 µs. For laser transitions, $^4G_{5/2} \rightarrow {}^6H_{9/2}$ (in the red) and $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (in the orange), the luminescence branching ratios $\beta_{JJ'}$ are 40.2% and 33.8%, respectively.

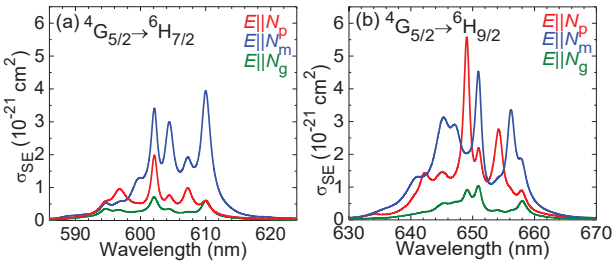

Fig. 2. Polarized stimulated-emission (SE) cross-sections, σ_{SE}, of Sm^{3+} ions in the $KGd(WO_4)_2$ crystal: (a) orange, the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition; (b) red, the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition.

The stimulated-emission (SE) cross-sections, σ_{SE}, for orange and red Sm^{3+} emissions were calculated using the Füchtbauer-Ladenburg equation based on the measured polarized luminescence spectra and the τ_{rad} and $\beta_{JJ'}$ values derived from the mJ-O theory. The σ_{SE} spectra exhibit a strong polarization anisotropy which is a prerequisite for linearly polarized laser emission, as shown in Fig. 2. For the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition, the peak σ_{SE} is 5.59×10^{-21} cm^2 at 649.0 nm and the emission bandwidth (FWHM) is 1.4 nm (for $\boldsymbol{E} \parallel N_p$). For the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition, the SE cross-sections are lower, with a peak value of 3.95×10^{-21} cm^2 at 610.0 nm and an emission bandwidth of 2.1 nm (for $\boldsymbol{E} \parallel N_m$).

The RT luminescence decay curves from the $^4G_{5/2}$ Sm^{3+} state were measured for different doping levels, see Fig. 3. For 0.4 at.% Sm^{3+}, the luminescence decay is nearly single exponential in agreement with a single type of sites for the dopant ions (C_2 symmetry), and the luminescence lifetime is 719 µs in good agreement with the radiative one. On increasing the doping level (*i.e.*, decreasing the distances between the active ions), the cross-relaxation processes ($^4G_{5/2} + {}^6H_{5/2} \rightarrow {}^6F_J + {}^6F_{J'}$) between adjacent Sm^{3+} ions are enhanced leading to luminescence quenching and non-single-exponential decay.

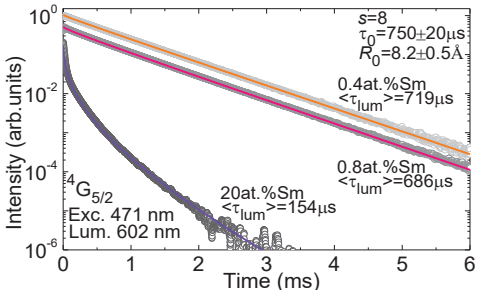

Fig. 3. Luminescence decay curves from the $^4G_{5/2}$ Sm^{3+} state in the $KGd(WO_4)_2$ crystal for various doping levels, *circles* – experimental data, *curves* – fits using the Inokuti-Hirayama model.

The decay curves were fitted using the Inokuti-Hirayama model for multipolar interactions [4], yielding the best-fit parameters τ_0 = 750 µs (the intrinsic lifetime), R_0 = 8.2 Å (the critical distance for energy transfer), and s = 8 (the parameter for dipole-quadrupole interactions). The average luminescence lifetime $<\tau_{lum}>$ decreased to 686 µs for 0.8 at.% Sm^{3+} and further to 154 µs for 20 at.% Sm^{3+}.

4 Conclusion

To conclude, Sm^{3+}-doped $KGd(WO_4)_2$ crystals are appealing for the development of visible lasers due to (i) relatively broad absorption around ~480 nm, (ii) high SE cross-sections with a strong polarization-anisotropy in the red and orange spectral ranges, (iii) a relatively long luminescence lifetime of the $^4G_{5/2}$ metastable state and weak luminescence self-quenching via cross-relaxation. Further evaluation of the potential of these crystals require the study of excited-state absorption (ESA) in the visible.

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References

1. C. Kränkel, D. T. Marzahl, F. Moglia, G. Huber, P. W. Metz, Laser Photonics Rev. **10**, 548 (2016).
2. P. Loiko, D. Rytz, S. Schwung, P. Pues, T. Jüstel, J.-L. Doualan, P. Camy, Opt. Lett. **46**, 2702 (2021).
3. P. Loiko, A. Volokitina, X. Mateos, E. Dunina, A. Kornienko, E. Vilejshikova, M. Aguilo, F. Diaz, Opt. Mater. **78**, 495 (2018).
4. M. Inokuti, F. Hirayama, J. Chem. Phys. **43**, 1978 (1965).